ELSEVIER

Effect of intermolecular interactions on the plastic deformation of glassy polymers

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The difference in molecular motion between shear plastic deformation and craze yielding for glassy polymers was analysed using polycarbonate (PC) and poly(methyl methacrylate) (PMMA) of different molecular weight, and PC blended with a methyl-methacrylate-based copolymer. These samples differed from one another in their intermolecular interactions. It was suggested that the criterion for shear yield was independent of the molecular weight, and that the stress for nucleation of internal crazing increased with an increasing molecular weight. It was concluded from these results that craze yielding is accompanied by a slip between oriented molecular chains around voids resulting from high dilatational stress, in contrast to the shear plastic deformation which is caused only by the rotation of small segments in the molecular chain.

(Keywords: glassy polymer; craze; shear yield stress)

INTRODUCTION

It is well known that glassy polymers can be plastically deformed by shear yielding and crazing[1-3]. In shear yielding, the volume of material is held constant, while on the other hand, crazing is accompanied by volume expansion[4] and can be regarded as an unstable local plastic deformation[5]. Several mechanisms have been proposed to account for the plastic deformation of glassy polymers[6-8]. The molecular theory proposed by Argon[7] for distortional plasticity gives a good explanation of the plastic deformation of a glassy polymer resulting from shear yielding. This description is based on the thermally activated production of molecular kink pairs which incrementally align short molecular segments and thereby produce strain. For crazing, this process is described as a micromechanical problem of the elastic–plastic expansion of initially stable micropores[5,9]. In these modes of plastic deformation for glassy polymers, it has already been pointed out that the criterion for yielding is influenced by intermolecular interactions such as the entanglement of molecular chains[10,11].

The purpose of this present paper is to examine the effect of intermolecular interactions on the shear plastic deformation and crazing in glassy polymers and to discuss the difference in molecular motion in both of these forms of plastic deformation.

EXPERIMENTAL

Preparation of specimens

The entanglement between the molecular chains can be the strongest interaction in a variety of intermolecular chain interactions[10,11]. In this study, the intensity of the intermolecular interactions is controlled by the state of entanglement. *Table 1* shows the samples used in this study. Three commercial grades of poly(methyl methacrylate) (PMMA) (Mitsubishi Rayon Co. Ltd) and polycarbonate (PC) (Teijin Chemicals Co. Ltd) with different molecular weights were examined in order to examine the effect of molecular chain length on both craze stress and yield stress. Since, in a large number of glassy polymers, the rubbery plateau modulus is constant regardless of the molecular weight[12], it can be presumed that the entanglement molecular weight is independent of the overall molecular weight. Therefore, the number of entanglements in a certain molecular chain increases with increasing the molecular weight. It has already been suggested that the density of entanglement increases with increasing the stiffness of the molecular chain; in other words, the molecular weight between entanglements decreases with increasing the stiffness of the molecular chain[11]. Polycarbonate, which has a rigid stiff molecular chain, in comparison to that of poly(methyl methacrylate), has a high density of entanglements. This density can be adjusted by using miscible blends of glassy polymers with different densities of entanglement[13]. The miscible blends[14] of PC with the methyl-methacrylate-based copolymer containing methyl methacrylate (70 wt%), tribromophenyl methacrylate (20 wt%), and cyclohexy methacrylate (10 wt%) ($M_n = 44\,500$; Kuraray Co. Ltd) are used to examine the effect of the density of entanglements. The parent PC was blended with the PMMA copolymer at various ratios resulting in blends with weight fractions ranging from 20 to 80 wt%. The PC and PMMA copolymer pellets were pre-mixed in a mixer and then melt-blended using a barrel temperature set at 533 K.

For PC and PC blended with the PMMA copolymer, sheets of 1 mm thickness for tensile testing were prepared

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Table 1 Molecular weights of the glassy polymers used in this study

Polymer	Molecular weight		
PC[a]	22 500	25 000	30 000
PMMA[b]	2×10^5	5×10^5	10×10^5
PMMA copolymer[b]		44 500	

[a] Viscosity-average molecular weight values are shown
[b] Number-average molecular weight values are shown

by compression moulding at 513 K. The PMMA used for tensile testing was in the form of commercial cast and excluded sheets with a thickness of 2 mm. Tensile specimens were prepared by milling into a rectangular shape with a width of 6 mm.

Specimens of PC and PC blended with PMMA copolymer used in the three-point bending tests were prepared on an injection moulding machine (Dyna-melter, MEIKI). The temperature of the cylinder was 533 K, at a moulding temperature of 353 K for PC, and 513 K, at a moulding temperature of 353 K, for PC blended with PMMA copolymer. The moulded specimens were isotropic except at their surfaces. The PMMA used for the three-point bending tests was in the form of a commercial cast and excluded sheet. The length of sample used for three-point bending of a round-notched bar was 50 mm for all specimens; the width was 12.4 mm for PC and PC blended with PMMA, and 10 mm for PMMA, while the thickness 6 mm for PC and PC blended with PMMA, and 5 mm for PMMA. The round notch, with a radius of 0.5 mm, was shaped by machining with a convex milling cutter. The ligament thickness, which indicates the specimen thickness at the notch, was 4.0 mm. The specimens were cooled with water during machine processing in order to prevent any rises in temperature. The specimens of PMMA were annealed for 24 h at 403 K in order to eliminate residual strain and were then quenched in ice.

Estimation of shear yield stress and stress for craze nucleation

In general, the stress for craze formation is estimated from the stress required to nucleate the surface crazing in uniaxial or biaxial tensile testing[15]. Therefore, the stress for the formation of crazing as estimated by such a method is limited to cases in which the stress for craze formation is lower than the uniaxial yield stress. We have already discussed the mechanism of the nucleation of internal crazing for several polymers with a higher stress for craze nucleation than the yield stress by using the three-point bending testing of a U-notched bar[16,17]. In this case, the stress required to nucleate the internal craze is introduced by the plastic constraint at the tip of the local plastic zone which is developed from the notch. There-fore, the nucleation of craze occurs on the inside of the polymer. The criterion for craze nucleation examined by this method is significant for the discussion of the relationship between the mechanism of the craze nucleation and the structure, as the nucleation of the internal craze is independent of the presence defects or contamination at the surface of the specimen, in contrast to the surface craze.

It was previously known that there is a maximum stress at the tip of the local plastic zone which spreads across the ligament thickness ahead of a round notch

under plane strain conditions[18]. When the stress ahead of the plastic zone reaches a critical stress as a result of the extending plastic zone, the development of the macroscopic craze, in which the plastic strain is locally concentrated between neighbouring microcrazes, occurs at the tip of the local plastic zone. If the stress ahead of the local plastic zone reaches a level which is equivalent to the strength of the fibrils, then the microrupture of the fibrils of craze leads to a catastrophic brittle fracture. The stress ahead of the local plastic zone developed from the round notch can be expressed by the following relationship:

$$\sigma_{\text{Pcrit}} = \tau(1 + 2\ln(1 + x/\rho)) \tag{1}$$

where σ_{Pcrit} is the mean stress ahead of the plastic zone, τ is the shear yield stress, x is the size of the plastic zone and ρ is the notch radius[18].

The shear yield stress was calculated from the uniaxial yield stress by dividing by $\sqrt{3}$; where the uniaxial yield stress was defined by the upper yield stress of the uniaxial stress–strain curve. Tests were carried out at a strain rate of $0.2 \, \text{min}^{-1}$ at 296 K. The stress for the nucleation of craze was estimated from the size of the plastic zone developed up to the nucleation of crazing by three-point bending tests on U-notched bars. The specimens were loaded at a bending rate of $2 \, \text{mm} \, \text{min}^{-1}$ with a span length of 40 mm. Mechanical tests were carried out on an Instron type testing machine (Auto Graph, Shimadzu DSS-5000). The selected temperatures for the tests were 296 K for PC, 313 K for PMMA and 343 K for PC blended with the PMMA copolymer.

Morphological analysis of deformation modes

In order to discuss the deformation processes of the U-notched bars in three-point bending tests under plane strain conditions, thin sections (thickness = $25–200 \, \mu\text{m}$) were cut perpendicular to the plane of the initial notch by using a microtome or micro-cutter. The morphologies of the crazes and plastic deformations were studied by using a polarizing microscope.

RESULTS

Effect of molecular weight on the shear yield stress and stress for craze nucleation

Figures 1 and *2* show the variation of the shear yield stress and stress for the nucleation of crazing as a function of the molecular weight. The dependence of the stress for craze nucleation of PC on the temperature is comparatively slight[9], while on the other hand, that of PMMA is quite sensitive in comparison to PC. In PMMA[17], a general yielding took place above a critical temperature and, in contrast, at low temperatures, brittle fracture was initiated from the notch tip. Therefore, the nucleation of internal crazing could be observed over a range of selected temperatures which is dependent on the molecular weight. The shear yield stress was nearly constant regardless of the molecular weight in all of the polymers examined. In contrast, it can be obviously seen from the experimental results that the stress for nucleation of the internal crazing increased with an increase in the molecular weight.

Effect of the density of entanglement on the shear yield stress and stress for craze nucleation
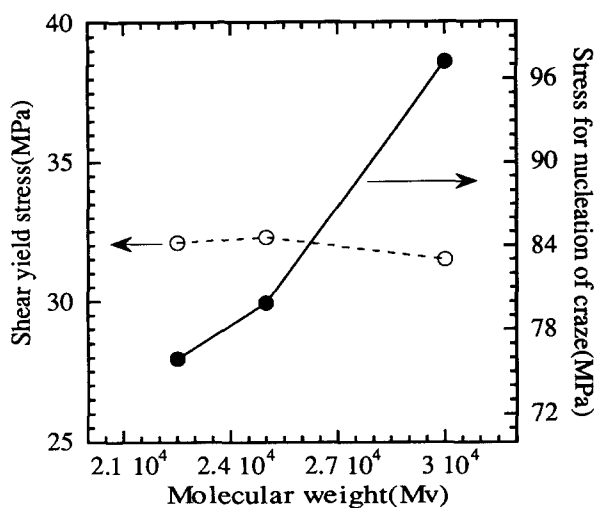
Figure 3 shows the bending moment–displacement

Figure 1 Variation of the shear yield stress and stress for craze nucleation of PC as a function of molecular weight
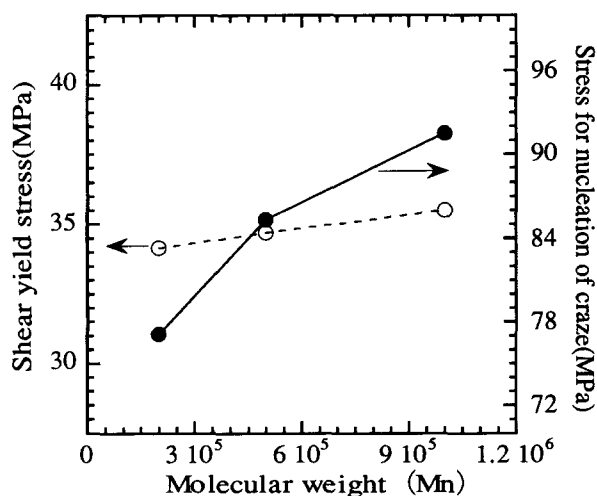

Figure 2 Variation of the shear yield stress and stress for craze nucleation of PMMA as a function of molecular weight
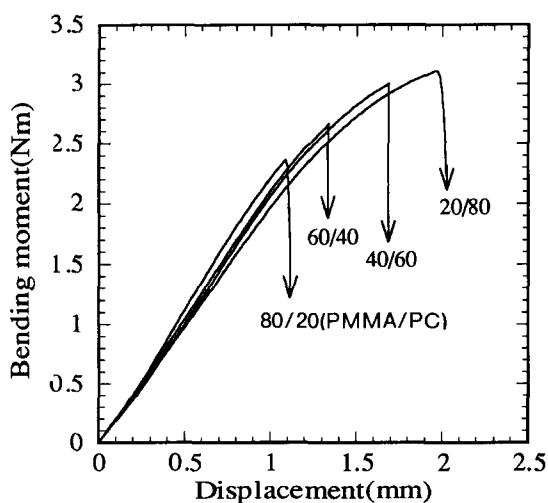

Figure 3 Bending moment–displacement curves of PC blended with PMMA copolymer as a function of PMMA copolymer content

curves of PC blended with PMMA copolymer as a function of the copolymer content. The molecular weight (M_v) of the PC used was 25 000. It can be obviously suggested that when the PC content was large, a high toughness of PC blended with PMMA copolymer was observed, and that the toughness of this blend decreased when increasing the content of the PMMA copolymer, the latter being a brittle polymer. *Figure 4* shows polarized photomicrographs of microtomed sections at the tip of the U-notch of PC blended with PMMA copolymer. When the content of the PMMA copolymer was high, the plastic deformation zone was comparatively homogeneous, although the mode of deformation became unstable on increasing the PC content. It is well known that the mode of plastic deformation for PMMA is stable at this temperature[17], while in contrast, that of PC is unstable (as shown by the presence of a shear band)[16]. It is interesting to note that the stability of the plastic deformation depends on the composition of the PC blend with the PMMA copolymer. *Figure 5* shows the variation of the shear yield stress and stress for the craze nucleation as a function of the content of the PMMA copolymer. It is understood that the stress of craze nucleation increases monotonically with increasing PC content, because the stress of the nucleation of crazing of the PC is higher than that of the PMMA copolymer. The variation of shear yield stress with the PMMA copolymer content also follows this compositional rule, as shown in *Figure 5*. It is already known that blends produced between PC and the PMMA copolymer are miscible below a certain critical temperature[14]. When the molecular weight of the PC used is large and the temperature of blending is high, a phase transition occurs. In this case, the variation of the shear yield stress and stress for craze nucleation as a function of the composition of the blend did not follow any compositional rule.

DISCUSSION

A characteristic feature of plastic behaviour in glassy polymers, differentiating it from ductile metals, is the strong molecular orientation hardening that occurs at a large strain, which results in a sharp upturn in the tensile plastic resistance curves[19]. The form of these curves is reminiscent of the large strain behaviour of crosslinked rubbers. This resemblance is real because of the almost complete recoverability of shape of highly distorted glassy polymers when they are heated to above their glass transition temperatures. These features suggest that the molecular process of plastic deformation is the rotation of small molecular segments, without the slip of molecular chains, as represented schematically in *Figure 6*. Therefore, the yield criterion is independent of the molecular weight, as shown in *Figures 1* and *2*. One such formalism is that of Argon[7,19]. In this approach, a specific form of strain-producing molecular segment rotation is conceived and the saddle-point free energy for this is calculated in terms of various molecular-scale parameters. This indicates that the plastic resistance is governed by the stiffness of the molecular chains which influences the density of entanglement.

Craze yielding is an unstable plastic deformation, similar to the necking which occurs in uniaxial tensile deformation[20]. In general, from a microscopic viewpoint,
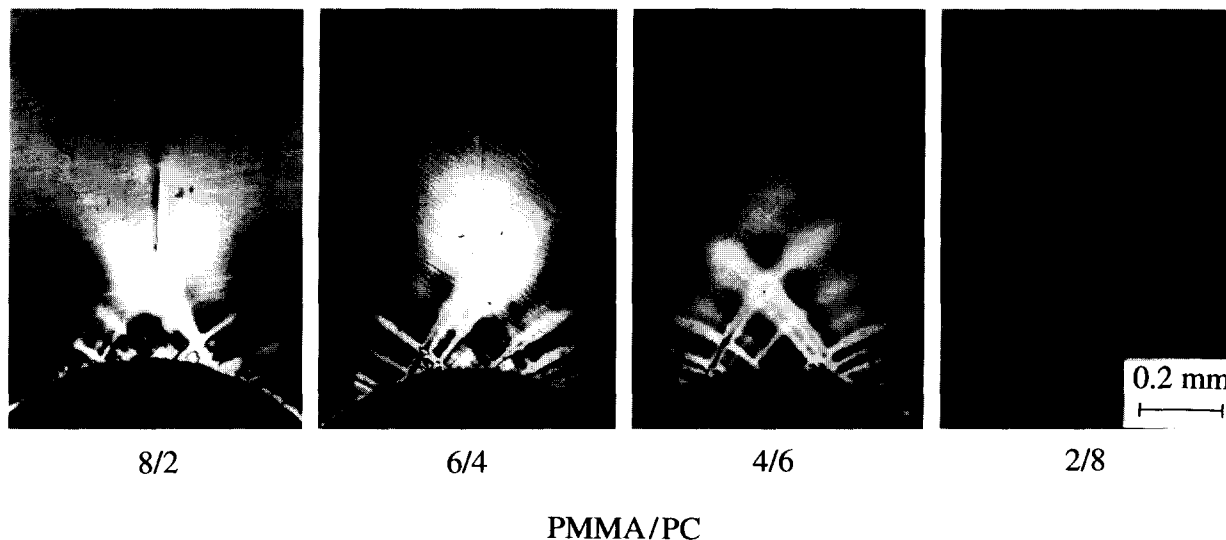
8/2   6/4   4/6   2/8

PMMA/PC

Figure 4   Polarized photomicrographs of microtomed sections at the tip of the U-notch of PC blended with PMMA copolymer
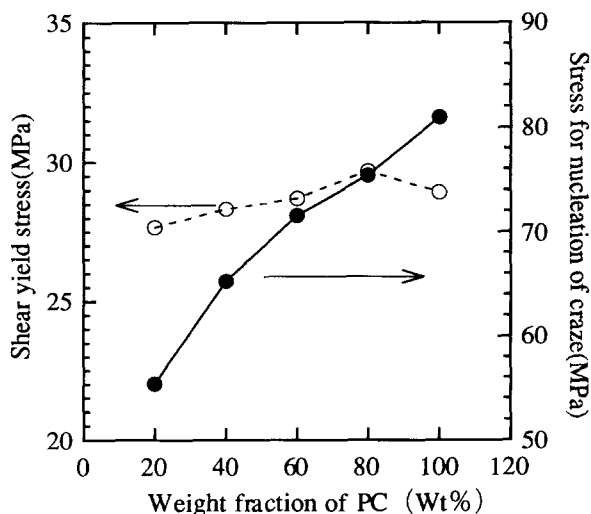

Figure 5   Variation of the shear stress and stress for craze nucleation of PC blended with PMMA copolymer as a function of PMMA copolymer content

Figure 6   Schematic representation of the alignment of polymer molecules by a plastic stretching process

a polymer has a heterogeneous structure and also a distributed cohesive strength. When a load is applied to such a material, microscopic fracture occurs at the point where the cohesion strength is weak, thus forming a microvoid. An increase in applied load causes an increase in the number of voids, and this further causes an expansion of these voids, with a corresponding circumferential plastic deformation of the latter. In this case, when the transferring speed of elastic strain energy stored in the material for expanding the voids is greater than that of the plastic deformation energy required to expand the voids, i.e. a mechanism similar to that of the brittle crack transmission theory of Griffith[21], the voids meet with an unstable plastic condition and expand rapidly. This is the mechanism of craze formation in polymers[20]. When the stress exerted on the crazes comprising oriented fibrils exceeds the strength of the fibrils, cracks are formed and brittle fracture occurs. The formation of crazes depends on various conditions, such as temperature, strain rate, and the structure of the
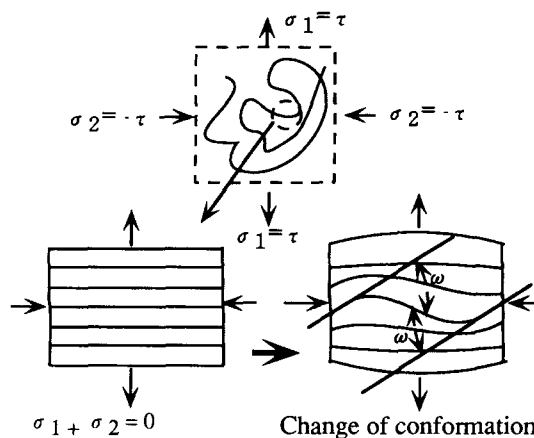
polymer. Although the crazing process obviously includes features of shear plastic deformation, the molecular-level requirement for the formation of voids is not yet well established.

Wu[10] has already concluded from the relationship between the stress required for surface craze formation and the density of entanglements for numerous glassy polymers that nucleation of voids is caused by the breaking of entanglements, and therefore the stress for craze nucleation depended on the density of entanglement[9]. Because the density of entanglements depends on the stiffness of the molecular chains, it is independent of the molecular weight. Therefore, the proposal made by Wu[10] means that the stress for nucleation of crazing is independent of the molecular weight. However, the experimental results obtained in this study obviously show that the stress of nucleation of internal crazing increases with an increasing molecular weight. It is well known that the viscosity of a melt polymer indicates the interaction between the neighbouring molecular chains over the chain length. Therefore, the viscosity of a polymeric material increases with increasing molecular weight. It can be suggested from the

σ_2

σ_1 Cavity σ_1

Slip between oriented σ_2 $\dfrac{\sigma_1 + \sigma_2 > 0}{}$
molecular chains
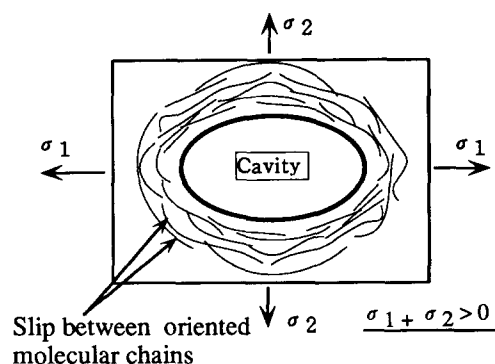
Figure 7 Schematic representation of the process of void formation prior to craze nucleation, which includes the slippage between oriented molecular chains

similarity of the molecular-weight dependence of the viscosity to that of the press required for craze nucleation that the process of void formation prior to this nucleation includes the slippage between oriented molecules around the voids due to high dilatational stress, in contrast to the shear plastic deformation (as schematically represented in *Figure 7*).

Furthermore, it can be proposed from the relationship between the stress for craze nucleation and the blend composition (as shown in *Figure 5*) that the resistance of slip between the oriented molecules depends on the density of entanglements, because the density of entanglements of PC is higher than that of PMMA[13,14].

CONCLUSIONS

The molecular motion of plastic deformation in glassy polymers was analysed by control of the state of entanglement. It was suggested that the criterion for shear yield is independent of the molecular weight, and

that the stress of nucleation of internal crazing increases with increasing molecular weight. It was concluded from these results that craze yielding was accompanied by a slippage between oriented molecules around a void as a result of high dilatational stress, in contrast to shear plastic deformation which was caused only by the rotation of small segments in a molecular chain.

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